

Assessment of Perchlorate Releases in Launch Operations

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14. ABSTRACT An overall approach to the assessment of potential perchlorate (ClO ₄ ⁻) releases from launch operations is presented. Two particular aspects of the assessment have been addressed to date. Laboratory studies to determine the effects of salinity and temperature on the chemical kinetics of perchlorate release from solid rocket motor propellant were conducted. The results showed an increase in the rate of perchlorate loss with increasing temperature and a decrease in the rate with increasing salinity. Second, a methodology developed for evaluating solid rocket motor propellant dispersal in the event of a catastrophic failure was applied to several failed historic launches as well as to Delta IV and Atlas V cases.				
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1. Introduction

1.1 Background

Ammonium perchlorate (NH_4ClO_4) is a commonly used oxidizer in solid rocket motor (SRM) propellants. Solid propellant missile motors and space launch vehicle motors typically contain approximately 70% NH_4ClO_4 by weight. The most common fuel used with NH_4ClO_4 is aluminum. Two other similar but less commonly used oxidizers are potassium perchlorate (KClO_4) and sodium perchlorate (NaClO_4). Other applications of ammonium perchlorate include certain fireworks and munitions.

The United States Environmental Protection Agency (U.S. EPA) has recently identified the perchlorate ion (ClO_4^-) as a contaminant in the environment originating from the salts NH_4ClO_4 , KClO_4 and NaClO_4 . The perchlorate ion is soluble in water and very mobile in aqueous systems such as groundwater. It is relatively unreactive and thus can exist for decades under typical groundwater or surface water conditions. Human health concerns focus on thyroid uptake of perchlorate, which results in reduced thyroid hormone production. Studies are currently underway to evaluate short-term and cumulative effects on other animal species as well as perchlorate uptake by plants. Only since 1997 have analytical methods to detect low-level perchlorate concentrations in water been available. More information and references on drinking water contamination, analysis techniques, and human health studies can be obtained elsewhere¹ including the U.S. EPA's Office of Ground Water and Drinking Water,² which has organized an Interagency Perchlorate Steering Committee (IPSC).

Appendix 1 contains a memorandum (dated Mar 2 2001) from the U.S. EPA, Region 9, containing information on current perchlorate contamination sites in the U.S.. According to the memo, there is no standardized approach to collecting or reporting perchlorate contamination data nationwide. The information in the memo was gathered from various sources with different protocols. However, the EPA states that perchlorate is "being found in water systems in nearly every type of climatic regime in the U.S.." Table 1 of Appendix A lists the occurrences and potential sources of perchlorate releases to the environment as of November 2000. Two figures are included with the memorandum: the first identifies U.S. perchlorate manufacturers and users; the second shows confirmed U.S. perchlorate releases. Suspected sources of the contamination include rocket manufacturing, rocket research, rocket testing, and propellant handling. The confirmed releases include at least one site where identified pieces of propellant containing perchlorate were retrieved from the soil.

Due to the widespread contamination of drinking wells in California (CA), the state added perchlorate to its list of unregulated monitoring requirements in 1999, and the CA Department of Health Services has reported testing from over 3000 wells. Because of such efforts, the majority of the Appendix 1 list is related to drinking wells or water supplies with some measurements in soils.

1.2 Launch Operations and the Potential for Perchlorate Releases

The current assessment of perchlorate releases in launch operations, initiated by the U.S. Air Force (AF) Space and Missile Systems Center and the Aerospace Corporation in 2001, addresses the potential impacts to areas where space launch and missile launch operations occur. These sites include but are not limited to launch overflight areas in the vicinity of Vandenberg Air Force Base (VAFB), Cape Canaveral Air Force Station (CCAFS), Kodiak Launch Complex (KLC), the Central Pacific Island Broad Ocean Area near Kwajalein Missile Range (KMR), and other broad ocean areas (BOA) in the Atlantic and Pacific.

Within or near each Department of Defense (DoD) launch site, Federal- and State-listed endangered species, habitats for endangered species, and/or Essential Fish Habitats occur. Each of these can potentially be impacted by perchlorate releases from launch operations. Although initial studies of perchlorate contamination focused on drinking water supplies, the observed persistence of the perchlorate ion is cause for concern with respect to contamination of other aspects of the environment. Neither short-term nor long-term impacts to microorganisms, fish and shellfish, corals, plants, marine mammals, fish, birds, or any other species are well characterized.^{1,2}

During recent environmental impact analyses conducted for AF programs, including the Evolved Expendable Launch Vehicle (EELV), the Quick Reaction Launch Vehicle (QRLV), and the Long Range Air Launch Target (LRLT), concerns regarding deposition of solid rocket propellant and associated perchlorate releases were raised. Agencies requesting or requiring data from the AF on perchlorate releases included the U.S. Fish and Wildlife Service, the Federal Aviation Authority, the National Oceanographic and Atmospheric Administration, and the U.S. Army. In addition to analyses and monitoring of short- or long-term perchlorate impacts, regulating agencies also requested documentation of solid propellant debris mitigation procedures for failed launches.

During normal DoD launches with solid rocket motors (SRMs), the solid fuel and oxidizer is burned to completion, and spent solid rocket motor cases are dropped in the ocean. It is generally assumed that only a small amount of residual unburned propellant is left in the spent cases. The National Aeronautics and Space Administration (NASA) Shuttle operation at Kennedy Space Center (KSC) is the only U.S. launch program that systematically retrieves their spent solid rocket boosters (SRBs) from the ocean.

In the event of failure of an SRM-containing missile or launch vehicle, the debris generated by the destruction of the system will include some unburned solid rocket propellant. When solid propellant is released by an accidental or intentional destruction of an ignited SRM, the propellant will continue to burn although at a slower rate than when contained in the motor. The amount of propellant surviving a launch failure depends on several factors including time after launch. Historically, failure follow-up investigations have focused on safety or operational issues rather than the quantification or retrieval of scattered solid rocket propellant. A method for quantifying the amount of propellant dispersed for a given launch failure is presented in Section 3, Launch Failures, of this report. Launch test programs that use non-ignited SRMs in drop tests can also release perchlorate when the unburned SRMs impact the ground or ocean.

1.3 Data Needs

A number of data and information needs with respect to potential perchlorate releases and impacts from launch operations have been identified. Figure 1.1 summarizes the current data needs and illustrates the interdisciplinary approach needed to determine whether there are significant perchlorate releases by launch operations and whether those impact the environment. For example, an understanding of potential cumulative impacts from perchlorate releases at a given launch site requires data on specific launch overflight areas, failure probabilities, biological habitats, species feeding and migration patterns, and fundamental chemical transport.

Existing data from legacy launch systems can be used to compile some of the data outlined in Figure 1.1, such as historic launch failure probabilities and locations previously impacted by debris. Other inputs, such as the detailed chemical kinetics of perchlorate diffusion from unburned solid rocket motor propellant fragments, require laboratory study. The scope of this current assessment has included an initial examination of launch failures, and the chemical kinetics of perchlorate release from propellant, but other subjects such as toxicity and feeding habits of species have not been addressed yet.

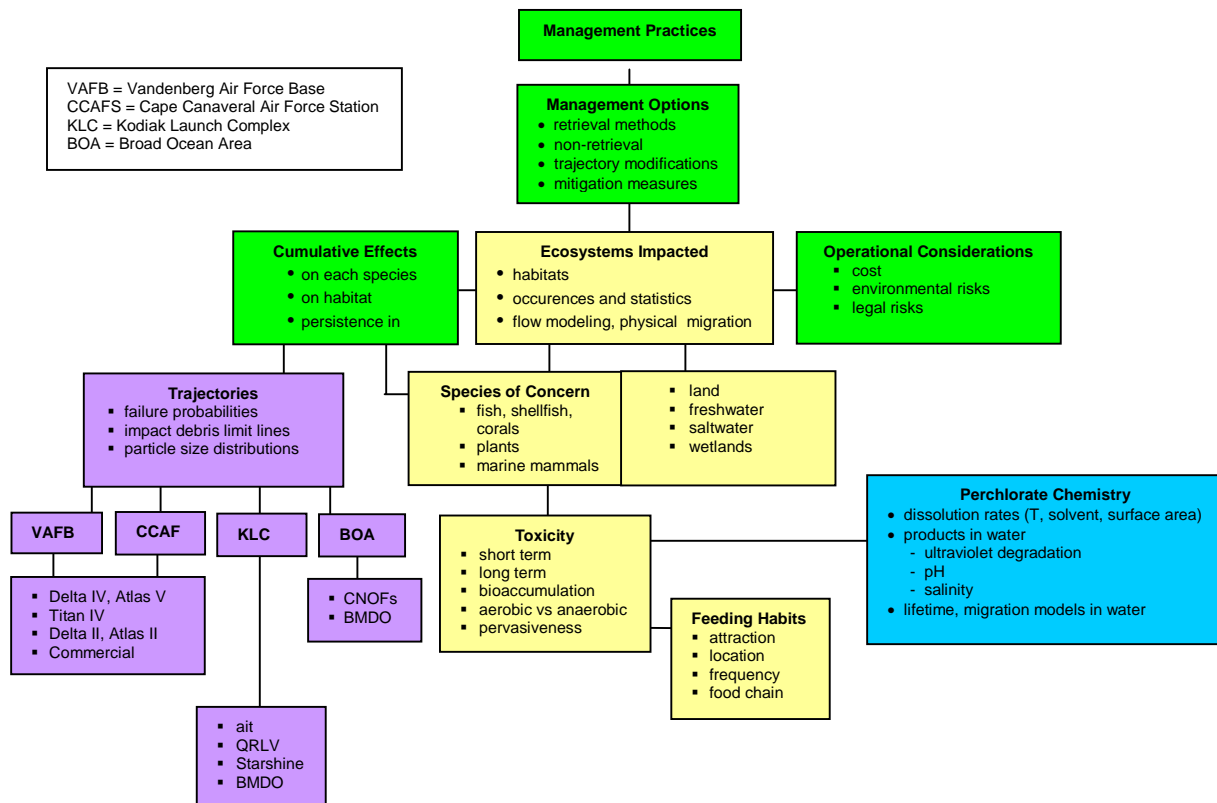


Figure 1.1 Interdisciplinary approach to assessment and management of perchlorate releases from launch operations.

1.4 Management of Potential Perchlorate Releases

The acquisition of DoD space launch systems is done in compliance with DoD Directive 5000.2R (dated June 2001), which requires programs to include environmental considerations in their systems engineering processes and to evaluate and consider environmental risks. The National Environmental Policy Act (NEPA) (42 U.S.C. 4321-4370d) and implementing regulations (40 C.F.R. 1500- and EO 12114) require all Federal agencies to assess the environmental impacts of their actions prior to the irrevocable commitment of any Federal resources. NEPA also requires that alternatives to the proposed action be considered. The goal of the current Assessment of Perchlorate Releases in Launch Operations is to provide some of the much-needed information and data to make informed decisions with respect to launch systems acquisitions, development, and operations. Figure 1.1 schematically illustrates how information from different disciplines can support good management practices with respect to potential perchlorate releases from launch operations. Operational practices are often determined by factors such as cost, safety, or mission considerations that must be weighed in combination with environmental (and associated legal liability) risks.

Specific examples of launch practices that could result in impacts from deposition of unburned propellant include:

- Use of unburned propellant in non-ignition tests
- Termination of launches over sensitive habitats or species of concern
- Non-retrieval of debris from launch failures

More generally, the choice of propellant and trajectory azimuth can affect the ultimate environmental impact of debris scattered during a launch failure.

Some examples of measures that could become part of management practices in the event of a launch failure are:

- Retrieval of unburned solid propellant
- Clean-up or deactivation of released perchlorate
- Non-retrieval of unburned solid propellant
- Trajectory modifications (e.g., added dog-legs or performance)
- Mitigation for species or habitat (e.g., wetland replacement)

Figure 1.1 illustrates how data from past launch failures, predictive models, biological studies, and chemical studies can contribute to well-informed decision making.

2. Chemical Kinetics of Perchlorate Release from Solid Rocket Motor Propellant

2.1 Background Chemistry and Previous Studies

The chemical formula of ammonium perchlorate is NH_4ClO_4 ; the formula weight is 117.49. Pure crystalline ammonium perchlorate is explosive; however, when diluted to 70% or less in water, it is completely ionized and is comparatively inert. Ammonium perchlorate solubility in water is $10.7\text{g}/100\text{ cm}^3$ at 0°C (about 1/3 the solubility of NaCl) and $42.4\text{g}/100\text{ cm}^3$ at 85°C .³ The perchlorate ion, ClO_4^- , formula weight 99.45, is the conjugate base of a strong acid so it has no influence on the pH of a dilute solution. The pH of aqueous solutions of ammonium perchlorate is acidic due to the ammonium ion (NH_4^+ , $K_a = 5.6 \times 10^{-10}$), so a 0.1 M solution has pH 5.1).

A typical solid rocket propellant containing approximately 65–75% ammonium perchlorate by weight also contains approximately 30% metal fuel (commonly aluminum), an organic binder (e.g., hydroxyl-terminated polybutadiene (HTPB), carboxyl-terminated polybutadiene (CTB), or polybutadiene acrylonitrile acrylic acid), a curing agent, and other compounds in lesser quantities, depending on the application.⁴

Some aspects of the effects of water and humidity on various solid propellants containing ammonium perchlorate have been previously studied.^{5–9} The details of some studies cannot be provided here because they are available only to U.S. Agencies (including DoD), and DoD contractors. A brief review of two of the studies follows.

A study by Merrill et al.⁵ included submerging samples of GEM II propellant into a swimming pool of circulating Pacific seawater. Samples were also placed in simulated seawater and in deionized water. Samples were 1-in., 2-in., 4-in., and 15-in. cubes. Some samples were buried in sand; the ammonium perchlorate leach rate was very close for buried and unburied samples. Unburied surfaces became slippery and slimy, possibly a result of biological activity. Samples swelled in volume with exposure time. Samples were dried after immersion to determine ammonium perchlorate loss by weight. Data is presented graphically. Crystals of ammonium perchlorate were observed on the outside of dried samples. Hazard tests on exposed then dried samples showed that the outer surfaces were less sensitive to friction and impact than virgin propellant, and the inner part was slightly less sensitive than virgin. Exposed samples would still burn when put into fire.

In a study by McIntosh et al.,⁶ which focused on recovering ammonium perchlorate from propellant, thin pieces of propellants TP-H1011 and ANB-3066, 1-in. x 1-in. with thickness of 0.2 to 0.006 in. were extracted with a high-speed propeller stirrer into a solution containing 14% ammonium perchlorate in water at 82°C (180°F) for 15 min. The solution also contained a dispersing agent. Recovery of ammonium perchlorate from the propellant was 96–98%.

In most previous studies, the focus was on either the effect of water on the propellant material properties, or on methods for recycling perchlorate. Some data exist on the diffusion constant for propellant in deionized water and on propellant weight loss in salt water. However, the database is lacking sufficient data for comparing the rate of perchlorate release from solid propellant immersed in fresh water and salt water at a range of temperature conditions.

2.2 Experimental

The purpose of this on-going study is to determine the rate at which perchlorate is leached from a propellant formulated with HTPB binder, and the effects of temperature and salinity on the rate. For this study, small pieces of solid propellant were held in individual containers and immersed in waters at temperatures near the range of seawater temperatures typically found from Alaska to Florida. The representative sea water temperatures are given in Appendix 2, Seawater Temperatures. Periodically, over the course of several weeks, the containers were opened, and the liquid analyzed to determine the concentration of perchlorate that had diffused from the propellant. Samples of propellant were immersed in water for a total of 1028 hours while held at a temperature of 5, 20, or 29°C.

Samples were prepared from Titan IV Solid Rocket Motor Upgrade (SRMU) HTPB-containing propellant, which had been obtained for a previous study from the Air Force Research Laboratory, Missile Technology Division, Edwards Air Force Base, California. Samples were prepared by blade-cutting and using a blade cork-borer tool. Samples are cylindrical in shape, with a height of approximately 14 mm and diameter of approximately 14 mm. The weight of each sample was approximately 4 g. Table 2.1 lists the sample identification numbers and exposure conditions, measured height, diameter, and weight and the calculated density and surface area.

Table 2.1. Sample Descriptions

Sample ID	Sample exposure condition	Weight (g)	Height (mm)	Diameter (mm)	Density (g/cm ³)	Surface Area (mm ²)
DH1A	Deionized water 29°C	4.22	14.90	14.05	1.828	967.8
DH2B	Deionized water 29°C	4.00	14.00	13.79	1.913	905.2
DH3F	Deionized water 29°C	3.71	13.09	13.73	1.915	860.7
DM1G	Deionized water 20°C	4.11	14.44	14.04	1.842	946.6
DM2C	Deionized water 20°C	3.70	12.78	13.65	1.979	840.7
DM3H	Deionized water 20°C	3.52	12.24	14.05	1.856	850.3
DC1I	Deionized water 5°C	4.15	14.63	14.11	1.814	961.2
DC2D	Deionized water 5°C	4.29	14.87	14.09	1.851	970.1
DC3N	Deionized water 5°C	4.05	14.46	13.94	1.836	938.5
SH1J	Salt water 29°C	4.37	15.03	13.88	1.921	958.0
SH2E	Salt water 29°C	3.73	13.04	14.13	1.828	892.5
SM1K	Salt water 20°C	3.61	12.85	13.76	1.889	852.9
SM2L	Salt water 20°C	4.17	14.45	14.22	1.817	963.2
SC1M	Salt water 5°C	3.66	12.57	13.80	1.949	844.1
SC2O	Salt water 5°C	3.97	13.82	13.99	1.870	914.8

Samples were immersed in 250 ml of deionized water or salt water. The salt water was simulated seawater made from a commercial product¹⁰ intended for seawater aquarium use. Actual seawater was not used because it contains biological elements with maintenance requirements beyond the scope of this study. Samples were not actively mixed while being held between analyses, but experienced some mixing effects as a result of vibrations from the temperature-control chambers. Samples were mixed immediately before the withdrawal of an aliquot for analysis. Samples were held at a temperature of 5, 20, or 29°C. Table 2.2 shows the temperature variations during the course of the study.

The concentration of perchlorate in the samples was measured using a perchlorate Specific Ion Electrode. The manufacturer's¹¹ recommended method for the determination of perchlorate was followed. The perchlorate in each sample solution was determined by comparing the reading of an aliquot taken from the sample container to the standard curve. An Ionic Strength Adjuster was added to standards and samples after dilution to known volume. Calculation was performed to correct for the dilution of the aliquot during the analysis, giving the actual concentration of the solution in the sample container at the time of analysis.

Fresh standards were prepared for each analysis. Standard curves were run with deionized water and with salt water to make sure that the salt from the salt water samples did not interfere with the operation of the perchlorate electrode. No interference was expected since the samples were diluted at least 1:10 prior to analysis. Within experimental error, no difference was found between the 1:10 diluted salt water and deionized water standards.

The repeated withdrawal of sample from the sample container reduces the liquid volume over time. To normalize each test for the increased concentration resulting from declining volume, the following steps were taken:

1. The total mass of extracted perchlorate was calculated from the current volume.
2. The total mass of the aliquot(s) removed for the analysis was calculated.
3. The sum of the total masses of aliquots removed for previous tests was calculated.
4. The sum of all the masses was the total that has been extracted at this point.
5. Dividing by the original sample volume at the start of testing gives the normalized perchlorate concentration.

Table 2.2. Temperature Conditions During Study

Average °C	Standard deviation	Minimum °C	Maximum °C
29.2	0.650	28.6	31.0
20.0	0.044	19.9	20.1
5.1	0.996	3.6	8.0

During the course of the study, one set of the raw data showed an inexplicable decline in perchlorate concentration. The perchlorate specific ion electrode was replaced, and subsequent results were within expected ranges. The two data points taken with the questionable electrode have been omitted from the data presented.

2.3 Results and Discussion

From the measurement of the concentration of the perchlorate ion in solution, the mass fraction loss of the propellant sample due to perchlorate leaching was calculated. Many previous studies inferred the perchlorate loss by performing weight measurements. In those studies, the total mass fraction loss of a sample would include, in addition to the mass fraction loss of perchlorate, the loss of the ammonium ion, the loss of the other water-soluble constituents, and the loss of insoluble constituents.

Table 2.3 shows the data for the mass fraction loss of perchlorate from the samples immersed in deionized water. Table 2.4 shows the data for the mass fraction loss of perchlorate from the samples immersed in salt water.

In Figures 2.1 and 2.2, the mass of propellant loss has been plotted against the square root of hours the sample was submerged in water. Table 2.5 gives the coefficients of the linear fits to sample data, as shown in Figure 2.2.

The highest rate of perchlorate loss is for samples in deionized water at 29°C. The lowest rate of perchlorate loss is for samples in salt water at 5°C. At each temperature, the rate for the salt water samples is slightly lower than that of the deionized water samples.

Table 2.3. Mass Fraction Loss Due to Perchlorate Leaching, Propellant Samples In Deionized Water

Hours	Temperature Sample ID	29°C DH1A	29°C DH2B	29°C DH3F	20°C DM2C	20°C DM1G	20°C DM3H	5°C DC1I	5°C DC2D	5°C DC3N
22		0.0497	0.0502	0.0511	0.0408	0.0392	0.0441	0.0265	0.0276	0.0276
66		0.0894	0.0906	0.0875	0.0662	0.0646	0.0638	0.0338	0.0327	0.0328
162		0.116	0.116	0.122	0.0796	0.0819	0.0780	0.0363	0.0353	0.0361
233		0.129	0.131	0.133	0.0970	0.0956	0.0959	0.0374	0.0374	0.0391
329		0.180	0.192	0.196	0.140	0.139	0.120	0.0437	0.0439	0.0447
376		0.176	0.158	0.174	0.114	0.116	0.115	0.0412	0.0459	0.0405
426		0.165	0.173	0.170	0.121	0.122	0.124	0.0451	0.0449	0.0458
498		0.183	0.218	0.209	0.153	0.143	0.158	0.0539	0.0528	0.0555
526		0.191	0.199	0.196	0.140	0.137	0.143	0.0493	0.0583	0.0573
569		0.195	0.197	0.202	0.149	0.148	0.159	0.0549	0.0563	0.0545
760		0.227	0.232	0.238	0.176	0.169	0.178	0.0589	0.0599	0.0623
833		0.211	0.214	0.214	0.160	0.159	0.163	0.0572	0.0568	0.0570
855		0.234	0.243	0.245	0.183	0.164	0.187	0.0653	0.0649	0.0673
909		0.247	0.253	0.264	0.181	0.189	0.202	0.0723	0.0719	0.0681
998		0.251	0.248	0.246	0.185	0.194	0.194	0.0673	0.0643	0.0693
1028		0.271	0.279	0.302	0.222	0.218	0.225	0.0832	0.0799	0.0805

Table 2.4. Mass Fraction Loss Due to Perchlorate Leaching, Propellant Samples In Salt Water

Hours	Temperature	29°C	29°C	20°C	20°C	5°C	5°C
	Sample ID	SH1J	SH2E	SM1K	SM2L	SC1M	SC2O
22		0.0488	0.0565	0.0422	0.0400	0.0315	0.0307
66		0.0706	0.0744	0.0540	0.0522	0.0321	0.0312
162		0.0814	0.0881	0.0613	0.0623	0.0304	0.0324
233		0.117	0.122	0.0872	0.0845	0.0413	0.0407
329		0.139	0.147	0.110	0.0950	0.0447	0.0439
376		0.114	0.125	0.090	0.0862	0.0355	0.0349
426		0.143	0.151	0.109	0.103	0.0459	0.0444
498		0.134	0.151	0.101	0.089	0.0397	0.0436
526		0.150	0.157	0.114	0.106	0.0410	0.0424
569		0.154	0.151	0.116	0.108	0.0461	0.0445
760		0.204	0.213	0.150	0.135	0.0562	0.0556
833		0.179	0.197	0.142	0.133	0.0535	0.0517
855		0.198	0.211	0.156	0.151	0.0590	0.0575
909		0.213	0.225	0.161	0.157	0.0641	0.0610
998		0.211	0.220	0.161	0.156	0.0614	0.0608
1028		0.228	0.245	0.182	0.160	0.0678	0.0641

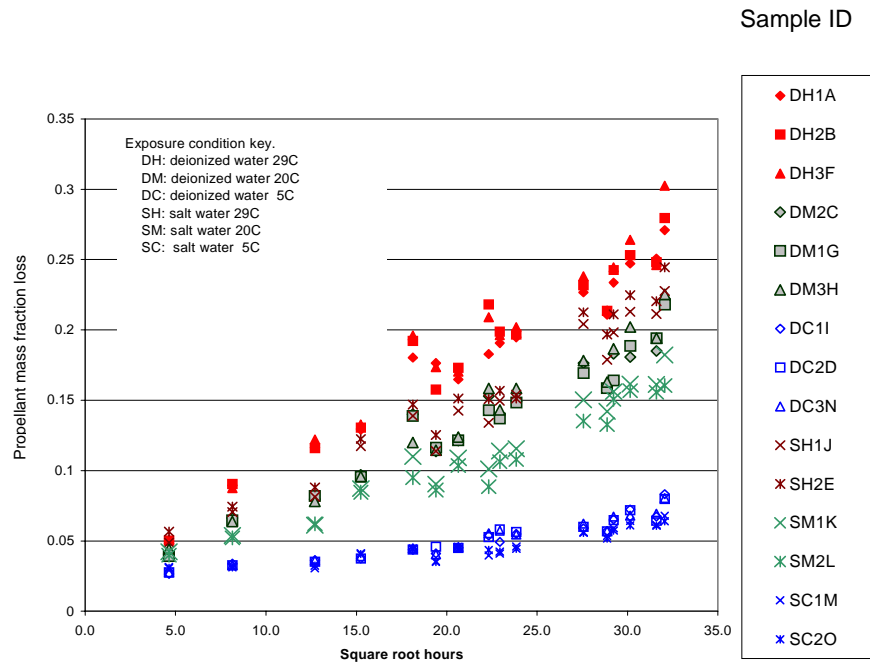


Figure 2.1. Propellant mass fraction loss vs. square root hours for several samples in deionized and salt waters at 29, 20, 5°C.

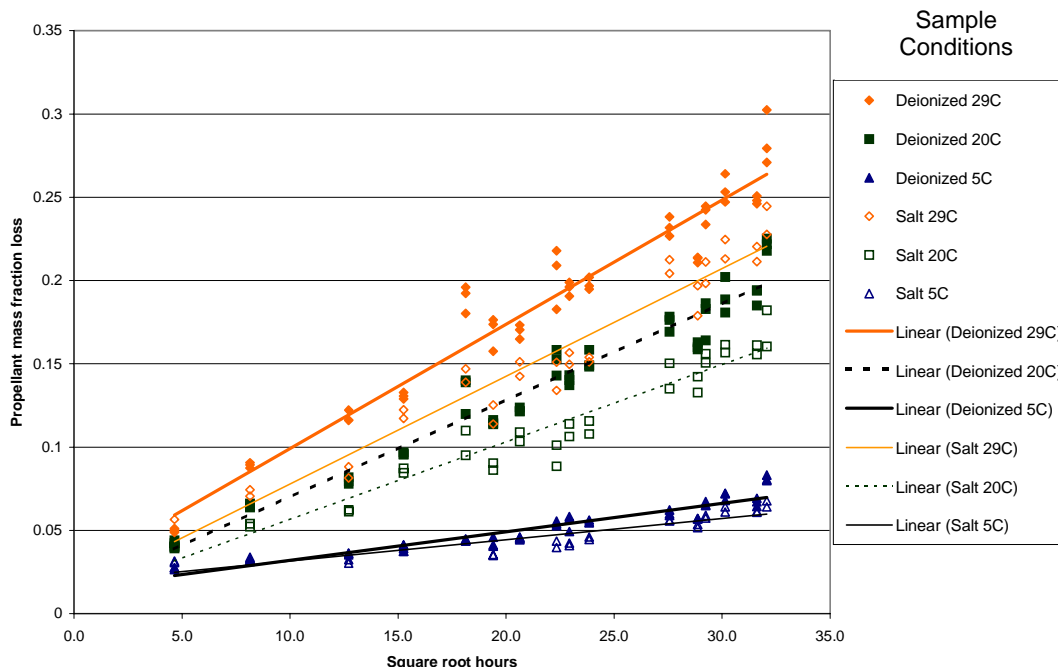


Figure 2.2. Linear least-square fit overlaid on propellant mass fraction loss of perchlorate with immersion time (square root hour) in deionized and salt waters at 29, 20, 5°C. Data from samples run under the same conditions are combined in this plot.

Table 2.5. Coefficients to Linear Fit of Mass Fraction Loss vs. Square Root Hours, for Each Exposure Condition

Sample type	slope	intercept
Deionized water		
29°C	0.00746	0.0246
20°C	0.00583	0.0117
5°C	0.00171	0.0149
Salt water		
29°C	0.00647	0.0131
20°C	0.00466	0.0099
5°C	0.00127	0.0189

The results show that higher temperatures correlate with faster perchlorate leach rates. Comparison of the rates at 29°C and at 5°C shows that the rate at the higher temperature is 4.3 times faster for samples in deionized water and 5.1 times faster for samples in salt water.

The effect of salinity is to reduce the rate of perchlorate loss from the sample. Table 2.6 shows a comparison of the rate for samples in salt water to the rate for samples in deionized water. Rates in salt water are roughly 15–25% slower than rates in deionized water. One factor may be viscosity differences. Diffusivities are inversely related to viscosity. Salt water has a higher viscosity than deionized water so a lower rate is expected.

Table 2.6. Ratio of the Rate of Mass Fraction Loss Per Square Root of Time for Samples in Salt Water Compared to Rate in Deionized Water

Temperature (°C)	Ratio of Rates
	$\left(\frac{\left(d_{\text{mass}} / d\sqrt{\text{time}} \right)_{\text{saltwater}}}{\left(d_{\text{mass}} / d\sqrt{\text{time}} \right)_{\text{deionized water}}} \right)$
29	0.868
20	0.800
5	0.745

The results shown in Figures 2.1 and 2.2 indicate that loss of mass of perchlorate from the sample is proportional to the square root of the exposure time. This indicates that the loss mechanism is a diffusion-limited phenomenon. The Einstein-Smoluchowski equation gives the root-mean-square distance traveled by a diffusing molecule.

$$(\Delta x)_{rms} = (2Dt)^{1/2} \quad (1)$$

In this equation, Δx is the distance traveled, D is the diffusion coefficient, and t is time. If the mass lost from the sample depends on the distance traveled by the diffusing molecules, this will result in the observed square root of exposure time relationship.

This could occur if the ions must diffuse to the surface of the sample to dissolve in the water, for example, or if the ions are released by water that diffuses into the sample. The mass loss mechanism will be discussed in more detail in a subsequent report.

Because of this proportionality to the square root of time, it is not possible to calculate a half-life for the extraction of perchlorate from the propellant. However, one can select an arbitrary endpoint and calculate the time to reach it by extrapolating from the data. If one defines an endpoint as 90% mass loss of perchlorate and assumes that the original ammonium perchlorate content of the propellant is approximately 70% by weight, the endpoint would correspond to a 0.533 mass fraction loss from the original sample. Table 2.7 shows the estimated time, extrapolated from the data based on these assumptions, for the samples at various conditions to reach the endpoint. This data cannot be extrapolated to other size pieces without consideration of factors such as surface area, mass, and volume.

Table 2.7. Estimated Time to Reach 90% Mass Loss of Perchlorate From Propellant Sample

Sample type	hours
Deionized water	
29°C	4700
20°C	8000
5°C	92000
Salt water	
29°C	6500
20°C	13000
5°C	160000

2.4 Summary

The rates of extraction of perchlorate from an HTPB-containing solid propellant immersed in waters of different salinity and temperature conditions have been measured. It was found that the extraction rate is consistent with a diffusion mechanism and is proportional to temperature and inversely proportional to salinity. The fastest extraction rate was observed at highest temperature and lowest salinity.

Data acquisition for this study is continuing, as well as a more thorough analysis of the data obtained to date. A suitable method for determining the diffusion coefficient¹² has been identified and will be applied to the experimental data. The activation energy will be calculated. Additional experiments with different solid-propellant formulations are being performed.

3. Launch Failure Analyses

In order to assess the potential impact of unburned solid propellant on sensitive species or habitats, it is necessary to determine the geographic extent of debris impacts from previous launch failures and to predict where debris is most likely to fall in the event of future failures. Failure probabilities can be estimated from both previous launch failure data and from semi-empirical predictive calculations. Historic launch failure data can also be used to examine whether any cumulative impacts are occurring at a particular launch site.

A brief history of DoD launch vehicle failures at CCAFS and VSAFB, the Eastern and Western Ranges, respectively, is provided in Section 3.1. Failures of suborbital vehicles, test targets, and other missiles that utilize NH_4ClO_4 -containing solid propellants are not included in Section 3.1, but should be considered in assessing total or cumulative solid propellant and perchlorate depositions.

Section 3.2 describes a methodology developed by The Aerospace Corporation to quantify the probability of solid-propellant impact over a particular region for any of the DoD legacy launch vehicles (Titan IV, Atlas IIAS or Delta II) or for Evolved Expendable Launch Vehicles (Delta IV or Atlas V). This methodology can be used to predict the mass of solid propellant (and thus perchlorate) that will be released if a failure occurs anywhere along the launch trajectory.

Section 3.3 describes another methodology and results recently used by TRW to compute probability density functions for debris impact from atmospheric interceptor technology program launches from the Kodiak Launch Complex. Although the results did not fully determine size distributions of solid propellant fragments, solid motor break-up modes, debris lists, and scatter plots were calculated. This type of information is useful in bracketing and locating the potential impacts from a failure.

3.1 Unmanned Space Launch Failures, 1983–2000

From 1983 to 2000, there have been a total of 16 unmanned space launch failures from the Eastern and Western Ranges (ER and WR), comprising approximately 5% of total launches. Fourteen of the failures were launch vehicles that had either a strap-on solid rocket motor (SRM) or core solid motors. Of those 14, only 6 failures occurred early in flight such that debris would impact within 100 nautical miles (nmi) of the launch pad (4 on ER, 2 on WR).¹³

A reconstruction of the solid-propellant debris field for a particular failure can be obtained by trajectory simulation modeling. Figures 3.1 and 3.2 show the likely debris patterns for the various recent near pad failures. These results assume approximately 2000 fragments with varying ballistic coefficients ranging from 50 to 250 psf with a randomly imparted velocity at the time of destruct. For this range of ballistic coefficients, wind effects would be minimal; therefore, zero velocity wind was assumed. That is consistent with SRM debris models used in Range Safety studies.¹⁵ Note that these plots also assume the solid propellant fragments to be extinguished at the time of vehicle destruct, and thus not burning on descent to ground/water impact. Observations and recovered debris from the

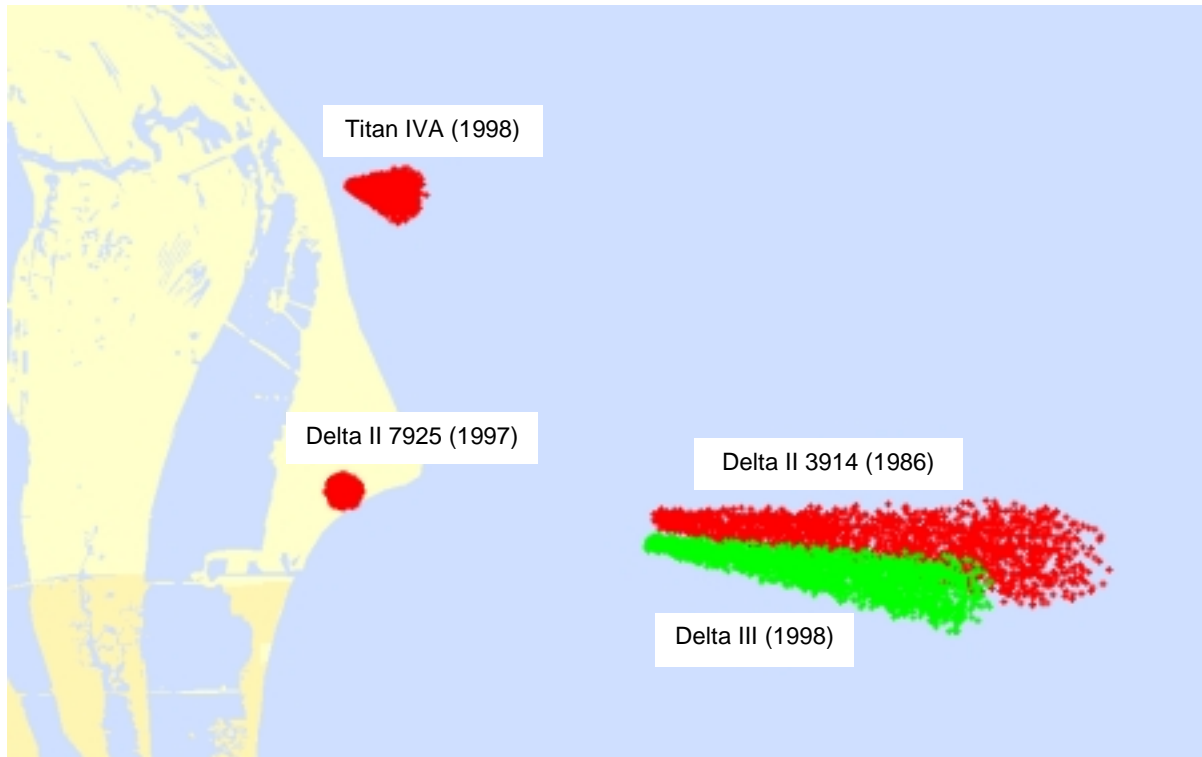


Figure 3.1. East-coast solid-propellant debris patterns (assuming no burning of debris).



Figure 3.2. West-coast solid-propellant debris patterns (assuming no burning of debris)

actual failures indicate that the propellant fragments do burn on descent, and, in fact, much of the solid propellant will burn up entirely during freefall. Therefore, the actual SRM debris patterns were probably smaller than what are shown in Figures 3.1 and 3.2, especially for the cases occurring further downrange.

The failure of a Delta II launch from CCAFS on 17 Jan 1997 provided some unique data on solid propellant survival. Launch anomaly follow-up procedures generally focus on safety aspects immediately following the incident and then on the failure investigation. Since solid propellant from the Jan 1997 failure washed up on a beach near the launch site, concerns over the safety of handling the propellant led to a study of propellant exposed to sea water.⁵ This study is described in Section 2.2. It was estimated that the amount of solid propellant debris in surf and ocean from the Delta II was no more than 4500 lb.¹⁴ Table 3.1 gives quantities of unburned propellant found during beach sweeps following the incident. A total mass balance of propellant estimated to have survived the failure was not available due to the broad area of land and ocean over which propellant was spread. Information is not available on how large an area was included in the beach collections summarized in Table 3.1.

While solid propellant ignited during a launch failure burns somewhat slowly under ambient pressure conditions, the above observations indicate that some fragments have survived past failures. If a failure occurs over water, rather than land, burning fragments will be extinguished and survive.

The degree of perchlorate diffusion out of fragmented solid rocket propellant depends in part on the fragment size (that is on the total surface area). Fragment sizes for the propellant found after the Jan 97 anomaly were not documented.

3.2 Probability Distribution of SRM Propellant Debris

For any launch vehicle containing solid propellant, there is a possibility that solid fuel will impact the region surrounding the launch site, the coastal waters, and downrange areas of the ocean. It is desirable to quantify the risk of such an occurrence to these regions. A methodology has been developed that estimates the probability of solid fuel impacting an area given a particular launch vehicle and a given launch azimuth. This study is similar to the failed launch scenarios described in the Essential Fish Habitat Technical Support Document¹⁶ prepared concurrently with the Supplemental Environmental Impact Statement for the Evolved Expendable Launch Vehicle 2000. However, the method

Table 3.1. Beach Sweep History, CCAFS, 1997¹⁴

Date (1997)	Quantity Solid Propellant Found (lb)
21 Mar	15
28 Mar	20
02 Apr	0
18 Apr	0
May	0
16 May	0
06 Jun	0
11 Jun	0
08 Aug	0

herein gives a probability that debris will land in a specified area, whereas the fish habitat study shows the areas that are in danger, without assigning a probability of impact. Also, the fish habitat study did not consider any ascent trajectory dispersions. Accounting for such dispersions results in a significantly larger potential impact region. The methodology has been applied to an east- and west-coast launch of the Delta IV-M(5,4) and an east-coast launch of the Atlas V(551).

3.2.1 Methodology for creating solid motor impact probability distributions

Given a particular vehicle and a particular flight azimuth, the methodology outlined will give the probability that solid debris will impact areas that are 30 arc seconds by 30 arc seconds for a single launch. This section describes the calculation of the probability of impact for three classes of solid propellant debris: less than 10 lb, 10–100 lb, greater than 100 lb. The results for each class are given in graphical form.

The probability of impact for a single class of debris landing on the i^{th} arbitrary area with crossrange (Δx) and downrange (Δy) dimensions can be written as:

$$P_{li} = \Delta t \times P_{Frate} \left(1 - \left(1 - \int_{x_i - \frac{\Delta x_i}{2}}^{x_i + \frac{\Delta x_i}{2}} \int_{y_i - \frac{\Delta y_i}{2}}^{y_i + \frac{\Delta y_i}{2}} f_i(x, y) dy dx \right)^{nfrag} \right), \quad (1)$$

where P_{li} is the probability of impact for the i^{th} area. Δt is the dwell time over the i^{th} area. P_{Frate} is the vehicle failure rate with units of 1/s. The terms x_i and y_i are the distance from the nominal impact point to the center of the i^{th} area. The term $nfrag$ is the number of fragments for a particular debris class. The term $f_i(x, y)$ is the probability distribution in the downrange (x) and crossrange (y) directions.

Equation (1) is applied to the midpoint between two discrete vacuum instantaneous impact points (IIP) obtained from the trajectory data. The vacuum IIP is where the vehicle would land if thrust terminated and it fell to the ground in a vacuum. Judgement is used to determine how close together these discrete points should be. For the early portion of the boost a 5 or 10-s interval is used. This 10-s interval is the dwell time, Δt .

The number of fragments ($nfrag$) is taken from the debris model. A debris model represents the pieces a vehicle will break up into after a failure. For this study, simplified versions of debris models are used in which only solid propellant fragments are included. The pieces of propellant are grouped into three classes: <10 lb pieces, 10–100 lb pieces, and >100 lb pieces. This study also contains the effects of propellant burning after the failure, so that beyond approximately 40 s into flight, there is no longer the possibility of significant solid propellant fragments impacting the ocean. Other important data obtained from the debris model are the ballistic coefficient and imparted velocity of the fragments, which are used to calculate the probability distribution of the debris.

The impact distribution ($f_i(x,y)$) is assumed to be a normal bivariate distribution in the crossrange and downrange directions. A Gaussian distribution is chosen because there are so many random events leading to a failure that it's impossible to predict what will happen. The standard deviations are based on wind dispersions, imparted velocity dispersions, malfunction turn data, and performance dispersions consistent with range safety probability studies.¹⁷

All of the parameters in Eq. (1) are taken from various sources and are different for each launch vehicle, and so each are specific to the case being discussed. Using launch vehicle trajectory data, vehicle failure rate, solid propellant debris model, and a Gaussian dispersion, an impact probability for a gridded region surrounding the IIP trace can be calculated.

3.2.2 Case studies

Three cases have been selected as examples: two Delta IV-M(5,4) missions and an Atlas V (551). The inputs for these case studies are the debris models, the failure probabilities, and the crossrange and downrange standard deviations as a function of time.

3.2.2.1 West-coast Delta IV-M(5,4)

The Delta IV-M(5,4) case consists of a Delta IV common core with 4 GEM 60 solid-propellant motors launched from VAFB, Space Launch Complex 6 (SLC-6). There are also variants of the Delta IV that have 2 GEM 60 solid motors, the second number in the parenthesis represents the number of solid motors. The launch azimuth for the chosen mission is 155°.

The debris model for the GEM 60s is shown in Table 3.2 as a function of time. This data is taken from Ref. 18, which is a debris model that takes into account the burning up of propellant as it falls to the ground. The ballistic coefficient and imparted velocity are used to calculate crossrange and downrange dispersions.

The failure rate used is $5 \times 10^{-4} \text{ s}^{-1}$; this is taken as an arbitrary value for the Delta IV first-stage reliability. It is approximately 3 times greater than the Delta II first-stage failure rate of $1.66 \times 10^{-4} \text{ s}^{-1}$.

The crossrange and downrange dispersions for debris impact are shown in Table 3.3. These values are based on Titan IV range safety data.¹⁷

These standard deviations are typically created by root-sum squaring of the dispersed impact locations due to winds, imparted velocity, vehicle guidance/performance errors, and vehicle malfunction turns. Three-sigma dispersions are calculated in the following manner. A launch vehicle trajectory modeling program is used to simulate a guidance error or malfunction turn to a destruct point, followed by fragment fall to ground impact. From a nominal point on the trajectory, a velocity is imparted in a direction to maximize the crossrange/downrange fragment impact distance. Similarly, from a nominal trajectory ascent, the fragment's fall is simulated in the presence of a 99% outer profile wind in the uprange, downrange, and left/right crossrange directions to determine the drag impact dispersion due to wind.

Table 3.2. Solid-Propellant Debris Model Over Time for Delta IV-M (4 SRMs)

Debris Class	Number of Fragments	Ballistic Coefficient (lb/ft ²)	Imparted Velocity (ft/s)
0–15 s			
<10 lb	624	106	169
10–100 lb	652	186	126
> 100 lb	332	285	100
15–25 s			
<10 lb	616	90	149
10–100 lb	196	181	119
> 100 lb	72	235-316	119
25–30 s			
<10 lb	584	68	141
10–100 lb	176	137	121
> 100 lb	58	176-221	121
30 – 35 s			
<10 lb	156	119	119
10-100 lb	36	149	119
> 100 lb	8	170-178	119
35 – 40 s			
<10 lb	8	161	120
10-100 lb	0	N/A	N/A
> 100 lb	0	N/A	N/A

Table 3.3. One-Sigma SRM Fragment Impact Dispersions Over Time

Debris Class	$\sigma_{\text{crossrange}}$ (nmi)	$\sigma_{\text{downrange}}$ (nmi)
0–15 s	0.5	0.5
15–25 s	0.7	0.8
25–30 s	0.9	1.1
30–35 s	1.1	1.3
35–40 s	1.3	1.5

From equation (1) all of this data is used to create Figures 3.3 through 3.11. These display the probability of impact for 30 arc-second by 30 arc-second cells. These plots show the probability distribution of solid fuel impact for a typical launch. It can be seen that the highest probability occurs very near the launch pad with the likelihood decreasing outward, generally in the shape of concentric ellipses. Note that the near pad values are in the 10^{-3} range, which approaches the overall failure probability for the launch vehicle for the first 40 s of flight ($5 \times 10^{-4} \text{ s}^{-1} \times \text{s}$). That is as expected. The impact probability vanishes downrange due to the assumption that all the fuel fragments will burn to depletion for failures after launch +40 s. Non-propellant debris fragments have debris patterns that extend beyond this time interval.

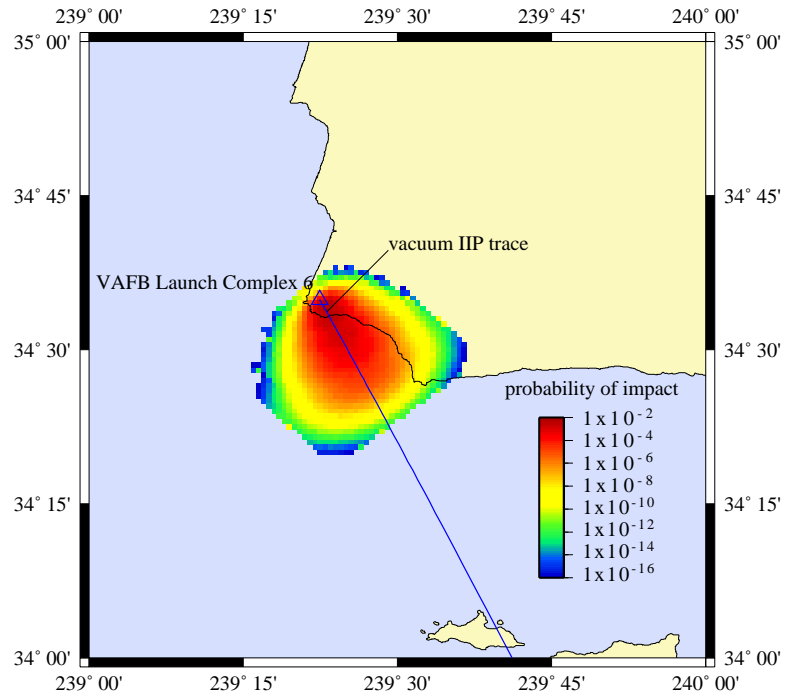


Figure 3.3. West-coast launch of Delta IV-M(5,4) probability of impact distribution for debris class of <10 lb for 30 arc-second by 30 arc-second cells.

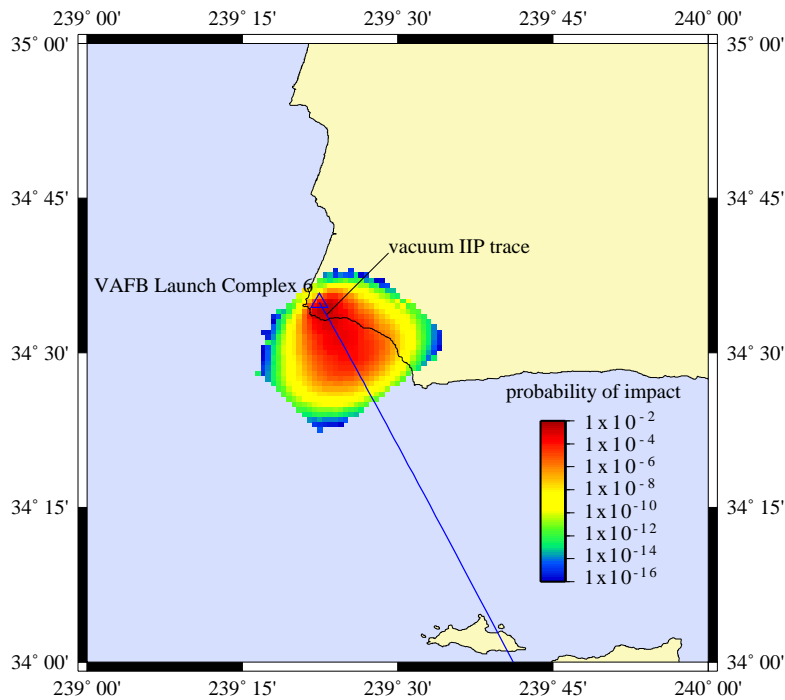


Figure 3.4. West-coast launch of Delta IV-M(5,4) probability of impact distribution for debris class of 10–100 lb for 30 arc-second by 30 arc-second cells.

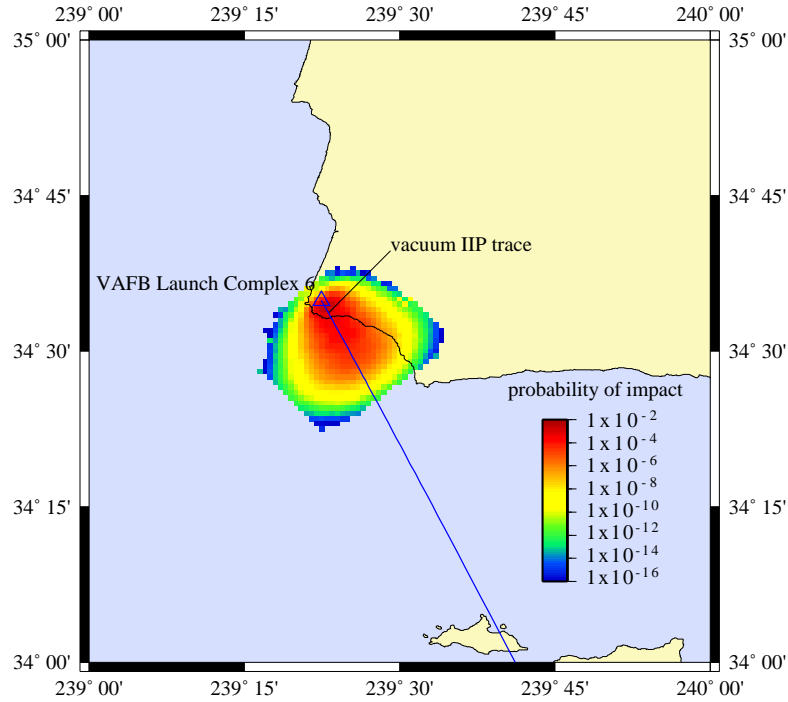


Figure 3.5. West-coast launch of Delta IV-M(5,4) probability of impact distribution for debris class of >100 lb for 30 arc-second by 30 arc-second cells.

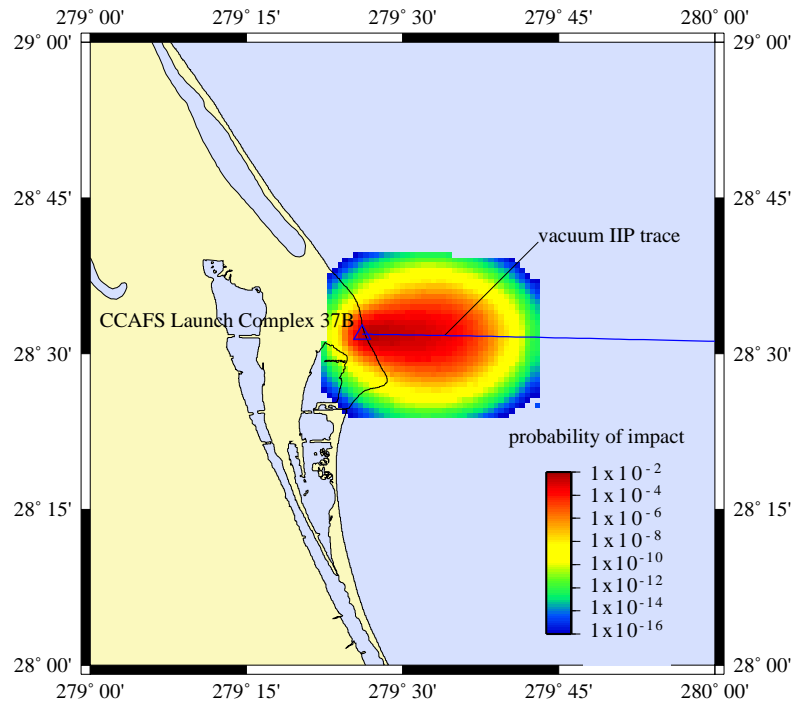


Figure 3.6. East-coast launch of Delta IV-M(5,4) probability of impact distribution for debris class of <10 lb for 30 arc-second by 30 arc-second cells.

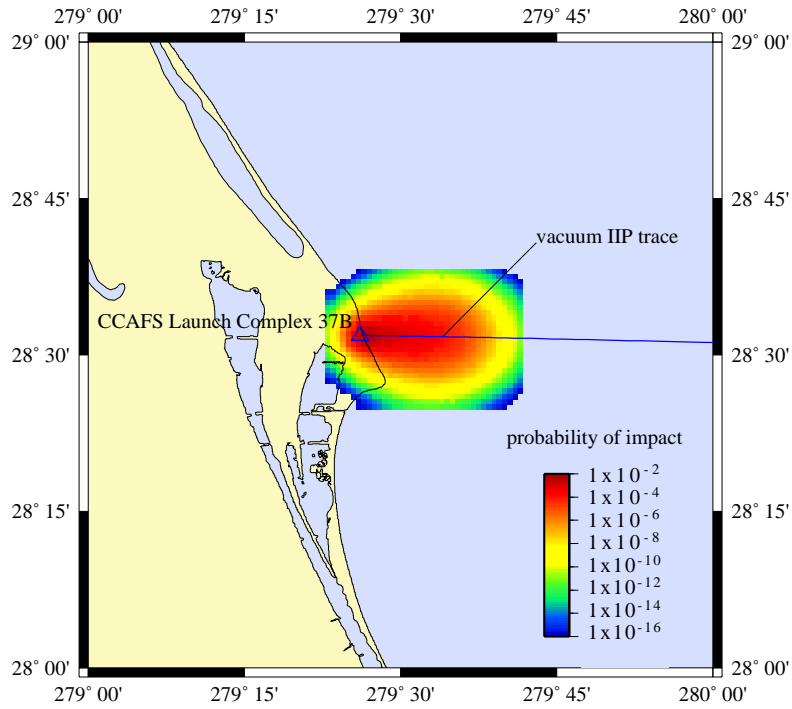


Figure 3.7. East-coast launch of Delta IV-M(5,4) probability of impact distribution for debris class of 10–100 lb for 30 arc-second by 30 arc-second cells.

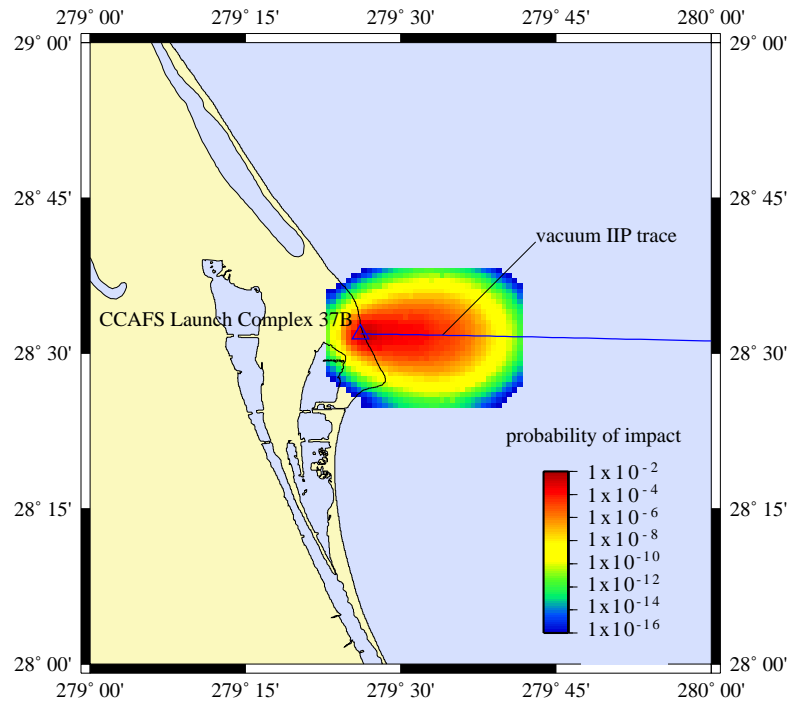


Figure 3.8. East-coast launch of Delta IV-M(5,4) probability of impact distribution for debris class of >100 lb for 30 arc-second by 30 arc-second cells.

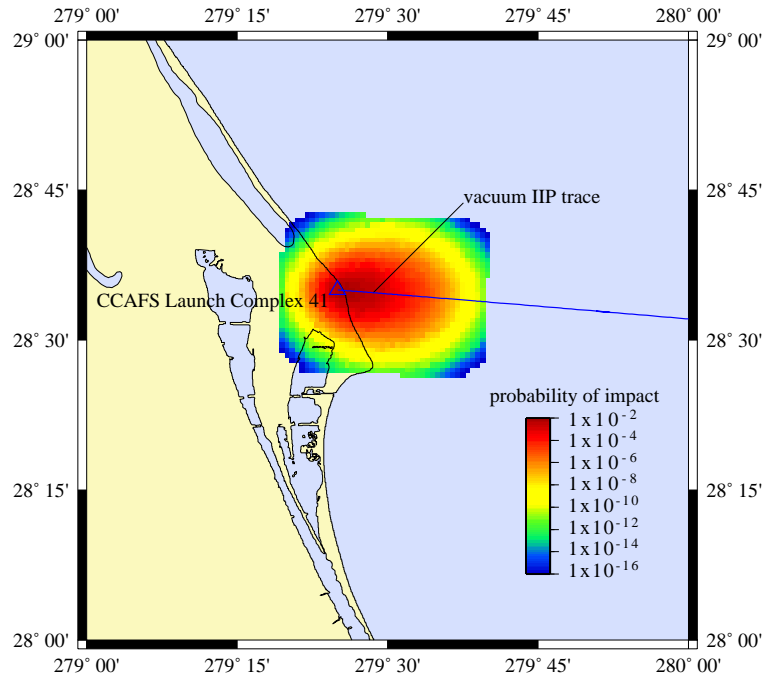


Figure 3.9. East-coast launch of Atlas V 551 probability of impact distribution for debris class of <10 lb for 30 arc-second by 30 arc-second cells.

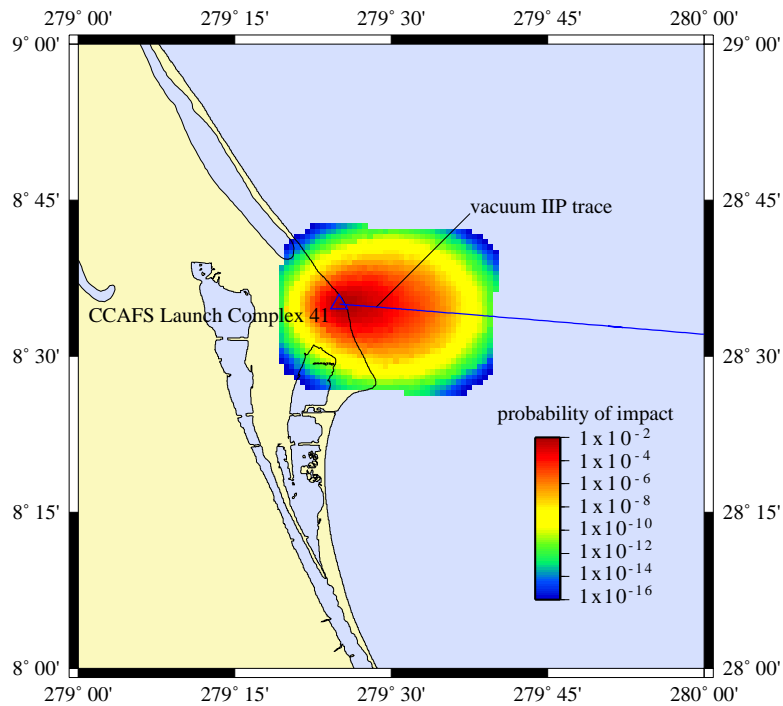


Figure 3.10. East-coast launch of Atlas V 551 probability of impact distribution for debris class of 10–100 lb for 30 arc-second by 30 arc-second cells.

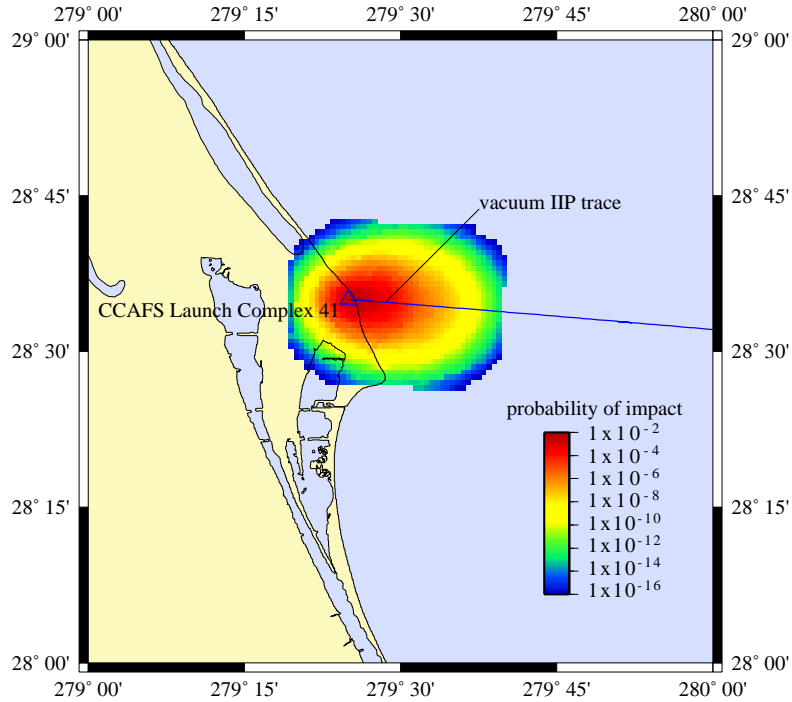


Figure 3.11. East-coast launch of Atlas V 551 probability of impact distribution for debris class of >100 lb for 30 arc-second by 30 arc-second cells.

3.2.2.2 East-coast Delta IV-M(5,4)

The launch azimuth is 95° , typical for a geosynchronous transfer orbit mission. Tables 3.2 and 3.3 also apply.

3.2.2.3 East-coast Atlas V 551

The launch azimuth is 95° , typical for a geosynchronous transfer orbit mission. Once again a vehicle failure rate of $5 \times 10^{-4} \text{ s}^{-1}$ was assumed. The debris and dispersions are given in Tables 3.4 and 3.5, respectively.

3.2.3 Using the results

The data created using this methodology is applicable only to these specific launch vehicles at these same flight azimuths. However, the results are very representative of a typical probability impact distribution for any launch vehicle that has SRMs. The major determining factors are the vehicle failure rate and the number of solid propellant fragments as a function of destruct time. If need be, these results can be scaled to be applied to similar vehicles with the same solids. An example would be to take the Delta IV-M(5,4) results and divide n_{frag} in Eq. (1) by 2 to represent the Delta IV-M(5,2), with the assumptions that the overall fragment number is one-half, and the same vehicle failure rate and a similar trajectory apply. The azimuths chosen are typical flight azimuths for the vehi-

Table 3.4. Solid Propellant Debris Model Over Time for Atlas V 551 (5 SRMs)

debris class	number of fragments	ballistic coefficient (lb/ft ²)	imparted velocity (ft/s)
0–10 s			
<10 lb	925	127	192
10–100 lb	885	230	141
> 100 lb	435	355	107
10–20 s			
<10 lb	920	61	257
10–100 lb	845	110	189
> 100 lb	370	219	171
20–30 s			
<10 lb	810	86	187
10–100 lb	245	166	184
> 100 lb	90	205	184
30–35 s			
<10 lb	55	146	195
10–100 lb	15	160	195
> 100 lb	0	N/A	N/A

Table 3.5. One-sigma SRM Fragment Impact Dispersions Over Time

debris class	$\sigma_{\text{crossrange}}$ (nmi)	$\sigma_{\text{downrange}}$ (nmi)
0–10 s	0.5	0.5
10–20 s	0.7	0.8
20–30 s	1.0	1.1
30–35 s	1.3	1.5

cle. Also, as the flight azimuth is rotated, the probability distribution would essentially rotate along with it according to the IIP.

3.3 Kodiak Launch Complex: atmospheric interceptor technology (ait) Program

To date, 3 sub-orbital Air Force launches have successfully occurred from the Kodiak Launch Complex, Kodiak, Alaska. NEPA Environmental Assessments (EAs) for the atmospheric interceptor technology (ait) Program and the Quick Reaction Launch Vehicle (QRLV) programs included estimates of areas that would be impacted by debris in the event of a launch failure.^{19,20} TRW simulations of launch failures provide numerical data and geographical data that can be applied to the determination of potential perchlorate releases from sub-orbital launch failures along trajectories out of KLC.²¹

The ait simulations produced scatter plots that show the debris impact locations plotted on a map of the launch area and the full downrange area, including the nominal ground track line for the mission and the debris limit lines. The TRW scatter plots²¹ are “intended to show the (deterministic or stochastic) position of every fragment for every failure mode for every time.” However, their utility would lie in selecting a particular launch time or debris type for detailed analyses with respect to

solid-propellant fragments. Event debris lists for ait and event descriptions also provide insight into the characteristics of solid-propellant fragments that would result from a failure of an SR-19 SRM, a typical motor used for KLC sub-orbital launches. The debris lists give dimensions of cylindrical SRM fragments. Based on photographs of terminated motors, it was assumed that the majority of the propellant stays bonded to the motor case during ejection. As the segments eject radially, it is predicted that they will break longitudinally into two equal fragments. For a single SR-19 stage, the TRW model predicted a total of 12 cylindrical segment motor-case fragments (case with bonded propellant).

For each debris item and failure mode, TRW also determined the probability that a particular debris item would land at a particular impact point or region. By summing all probabilities within a given region, an aggregate probability density function (pdf) is obtained. Given the location of a sensitive habitat area, the pdf can provide the statistical probability that debris will impact the area, a species, or even an individual. This approach was used to estimate potential impacts to endangered Steller's eiders for the Quick Reaction Launch Vehicle program.¹⁹ This information can then be used to predict short-term probabilities of ingestion of perchlorate-containing propellant fragments, perchlorate release rates, or long-term cumulative impacts.

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References

1. Urbansky, E.T. ed, *Perchlorate in the Environment*, Plenum Press, 2000.
2. www.epa.gov/ogwdw
3. *CRC Handbook of Chemistry and Physics*, 77th Edition" CRC Press Inc., Boca Raton, Florida 1996-1997.
4. G. P. Sutton and O. Biblarz, *Rocket Propulsion Elements*, 7th Edition, John-Wiley and Sons, 2001, pg. 496-497.
5. Merrill, C. I., Drobinak, J. D., "Sea Water Immersion of GEM II Propellant," Air Force Research Laboratory, AFRL-TR-ED-TR-1998-0034, Feb. 1999.
6. McIntosh, M. J., Shaw, G. C., Munson, W. O., Dinsdale, V. T., "Solid Rocket Propellant Waste Disposal/Ingredient Recovery Study," Final Report JPL contract 954161, 28 July 1975.
7. Easton, M.P., Lipeles, R. A., Adams, P. M., Genova, S. A., Ross, F. D., Katzman, H. A., Kao, W. H., "Effect of Water on HTPB Solid Propellant," *Proceedings of the 1999 JANNAF 28th Propellant Development and Characterization Subcommittee and the 17th Safety and Environmental Protection Subcommittee Joint Meeting*, 26-30 April 1999, CPIA-Pub 68 Vol II.
8. Davis, I. L., Carter, R. G., "Moisture Diffusion Degradation of Solid Propellant Properties," CPIA Pub-463, 1987 JANNAF Structures and Mechanical Behavior Subcommittee Meeting.
9. Marsh, B. P., Martin, D. L., "Moisture Diffusion in an HTPB Composite Propellant," CPIA-Pub-388, 1983 JANNAF Structures and Mechanical Behavior Subcommittee Meeting.
10. "Instant Ocean[®]" *Synthetic Sea Salt*, Aquarium Systems Inc., Mentor, Ohio.
11. Cole-Parmer Instrument Co., Niles, IL.
12. D .P. Shoemaker, C. W. Garland, J. I. Steinfeld, J. W. Nibler, *Experiments in Physical Chemistry*, McGraw Hill Book Co., New York, 1981.
13. Space Systems Engineering Database, The Aerospace Corporation, private communication, P. Cheng, 2001.
14. U.S. Air Force SPC 45th SW, private communication, J. Albury.
15. "LARA Vehicle Specific Databases," by M. Herndon & T. Naughton, ACTA, Inc., TR No. 97-350/5.1-02, September 1997.
16. "Essential Fish Habitat Technical Support Document for the Evolved Expendable Launch Vehicle Program Supplemental Environmental Impact Statement," by CH2M Hill, May 2000.

17. "Range Safety Probability Study; Titan IVB/NUS/WR," by P. Bernard, Lockheed Martin Corp., MCR-96-2535, March 1996.
18. "Delta IV and Atlas V SRM debris models," provided by ACTA, Inc.
19. "Final Environmental Assessment for the Quick Reaction Launch Vehicle Program," Department of the Air Force, Materiel Command, Space and Missile Systems Center, Jan 22, 2001.
20. "Final Environmental Assessment for the atmospheric interceptor technology Program," Department of the Air Force, Materiel Command, Space and Missile Systems Center, Nov 1997.
21. P. Salzman, "ait Hazards Analysis Final Report," TRW, 4 Nov 1996.



Appendix 1—U.S. EPA Region 9 Memorandum

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 9

**75 Hawthorne Street
San Francisco, CA 94105-3901**

March 2, 2001

MEMORANDUM

SUBJECT: Perchlorate Occurrence Table and Maps

FROM: Kevin P. Mayer, SFD-7-2

TO: Recipients of Perchlorate Maps and Table

This memo is meant to accompany a table of perchlorate occurrence and two maps produced EPA Region 9's GIS Center. These maps are entitled "U.S. Perchlorate Manufacturers and Users" and "U.S. Perchlorate Releases". The Table is entitled "Occurrence and Potential Sources of Perchlorate Releases to the Environment as of November 2000". The map of U.S. Perchlorate Releases displays the locations of the facilities listing in the table. All locations on the Releases map are also depicted on the Manufacturers and Users map, along with all other locations identified by the sources noted on the Manufacturers and Users map. The table and maps rely on information available to EPA in late November, 2000.

Information on Perchlorate Releases

The table and map of known perchlorate releases to the environment was an effort by contacts in all ten Regions of the U.S. Environmental Protection Agency to bring together the available nationwide information on where this chemical has been detected in the environment. The investigations that are the source of the data represent diligent and often ground-breaking efforts of state and local authorities as well as that of EPA offices.

Because the information was gathered for various purposes and with different and sometimes unspecified protocols, it is essential to explicitly explain what these data do and do not represent.

An Ongoing Effort to Communicate Information To-Date

We felt that it was important to begin the process of communication even if the initial result was incomplete or imperfect. We deliberately intended this document to spur corrections, additions or deletions of the information contained in the table. There has been no standardized approach to collecting or reporting perchlorate data nationwide.

We did intend to raise awareness that this hitherto unrecognized chemical is being found in water systems in nearly every type of climatic regime in the US. In some instances, perchlorate was unexpectedly detected in areas where no obvious perchlorate handling activities took place. In most others, perchlorate was found in the environment near facilities that were documented users or manufacturers of perchlorate salts.

Standards for Reporting Perchlorate Releases

We attempted to apply reasonable judgement in identifying “confirmed” releases and even in identifying “unconfirmed releases”. In California, public water supply wells must have detectable levels of perchlorate in at least two sampling periods before being considered actually detected. Most of the sites we listed from California and other states meet this criterion. At sites with many sampling points, multiple detections provided a preponderance of evidence that a perchlorate release had occurred. We omitted at least one site where perchlorate was detected once but not in subsequent sampling events. The American Water Works Service Company published a report (Siddiqui et al., 1998) identifying wells in their systems nationwide with perchlorate detections, and we included these locations even though we could not consider them confirmed. Resampling by AWWSC failed to detect perchlorate in a number of these wells. EPA Region 3 investigated the Yardley, PA, report from AWWSC but could not detect perchlorate in nearby groundwater. We felt it important to recognize this report but to note the lack of independent corroboration.

Perchlorate in soil posed another set of difficulties in reporting a site as having a confirmed release. Without a standardized sampling and analytical protocol, quantification of soil concentrations could be misleading and were omitted from the table. The solubility of perchlorate salts is so great that perchlorate-containing material found uncontained on the soil surface might reasonably be assumed to be contributing perchlorate to the subsurface through inevitable dissolution. We do have a number of sites where the association between soil contamination and groundwater contamination is strongly established. There are also sites where no water samples have yet been analyzed even though perchlorate has been detected in surface soils. The distribution of a solid perchlorate-bearing material on the soil surface may not be uniform. In at least one instance, identifiable pieces of a perchlorate-bearing propellant were gathered from the soil surface and is reported as a confirmed release.

Some Acknowledged Limitations

Obviously, few details or clarifying information can be contained in a single table much less in a single number. The table provides only a single maximum concentration value for any site. It is very possible that the information may not provide an accurate picture of any particular site. At some sites, samples have been collected for over three years at literally hundreds of monitoring points with fastidiously documented quality control. At others we have only a single monitoring point with perhaps only two water samples analyzed for perchlorate and no statistical evaluation is possible. The maximum value is not necessarily representative of the nature and extent of the perchlorate release for the site, and the maximum value may be much higher than any other value at that location.

Although many of the data originated from site-specific investigations, this document does not presume to definitively identify the facility responsible for the release nor the type of operation associated with the release. Some of the facilities are fairly isolated and have clear histories of perchlorate handling. Others facilities mentioned are reasonable possibilities based on current information. There are a few with completely unidentified sources - occasionally with several potential contributors.

Difference in Search Effort Throughout the United States

It is important to realize that the lack of perchlorate releases in a particular state or locality may merely reflect the absence of an effort to search for this contaminant. Neither the table nor the map indicates the extent of the investigation activities where perchlorate was not detected. Widespread monitoring efforts occurred in only a handful of states by the year 2000: Arizona, California, Iowa, Nebraska, New Mexico, New York (Suffolk County), Texas and Utah. Few perchlorate investigations have occurred in the eastern United States. Notable exceptions are at specific facilities in West Virginia, Maryland and the follow-up investigation in Pennsylvania. At the current state of knowledge, the distribution of perchlorate detections in the environment seems to be directly related to the effort put forth in searching for perchlorate.

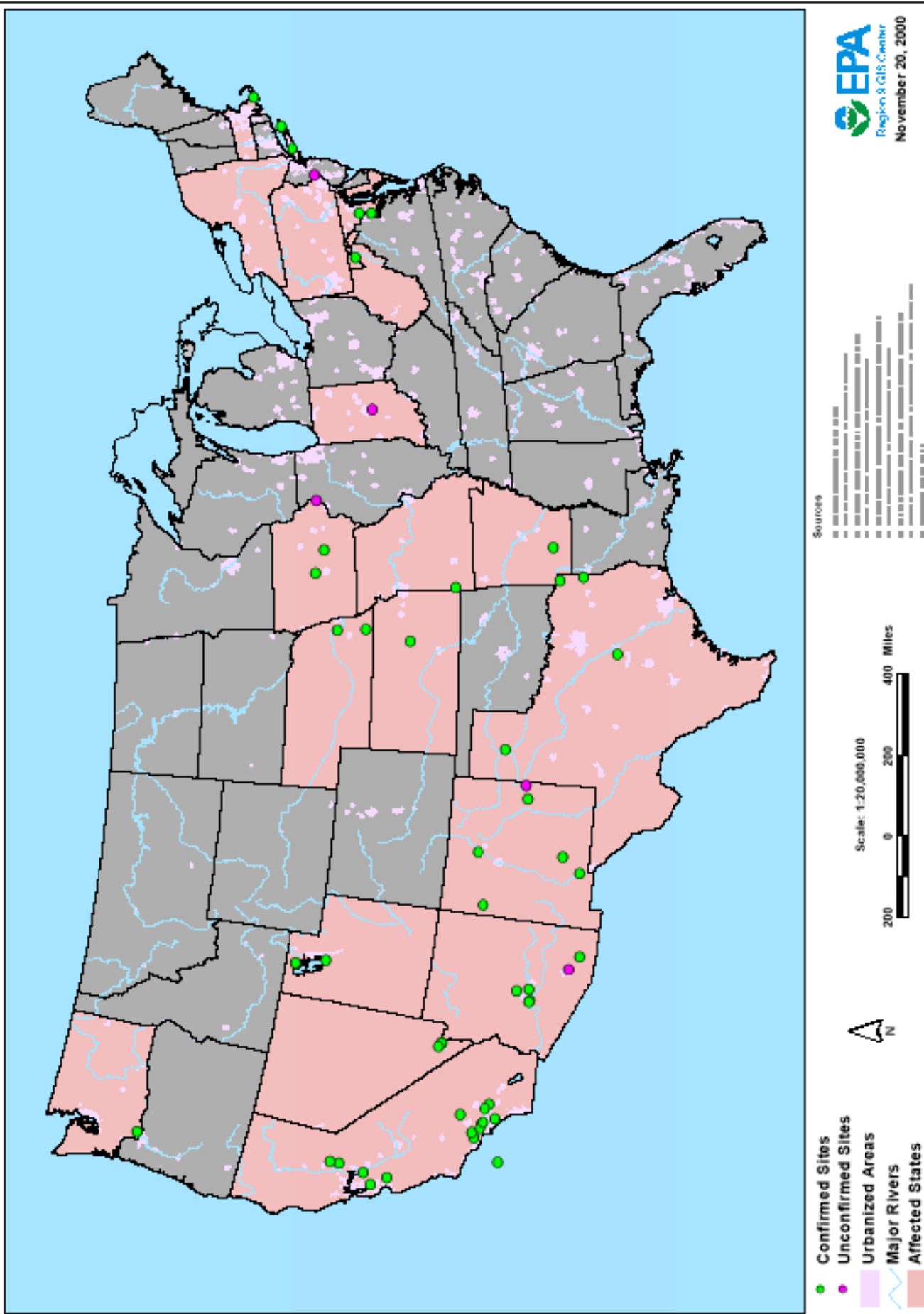
A high proportion of the locations on the current list of reported perchlorate releases were specifically targeted for perchlorate testing. Perchlorate manufacturers provided EPA with information on known purchasers of the raw material, and the Department of Defense also identified possible locations where perchlorate was handled. At a number of sites, State or federal cleanup activities were ongoing before perchlorate was identified as an environmental issue.

A few of the localized efforts to search for perchlorate should be noted. California added perchlorate to the list of unregulated monitoring requirements in 1999 and California Department of Health Services officials have reported results from testing over 2,000 public water supply sources in addition to more than a thousand monitoring wells tested around the state. In eastern Long Island, more than 500 wells - public, residential and monitoring wells - have been tested throughout Suffolk County. Utah tests approximately 60 public water supply wells in areas that may be affected by perchlorate handling facilities. Arizona officials have tested for perchlorate in water supply samples collected throughout the state and are involved in investigations at several facilities that have the potential for perchlorate releases. Several states are working with EPA's Region 7 to test rural wells for agricultural chemicals and added perchlorate as an analyte in approximately 30 locations in Nebraska and nearly 100 locations in Iowa. Texas and New Mexico officials are aggressively investigating for perchlorate at many likely sources, even beyond those facilities identified by perchlorate manufacturers and the Defense Department.

Please direct questions or comments to

Kevin Mayer

U.S. Perchlorate Releases



U.S. Perchlorate Manufacturers and Users

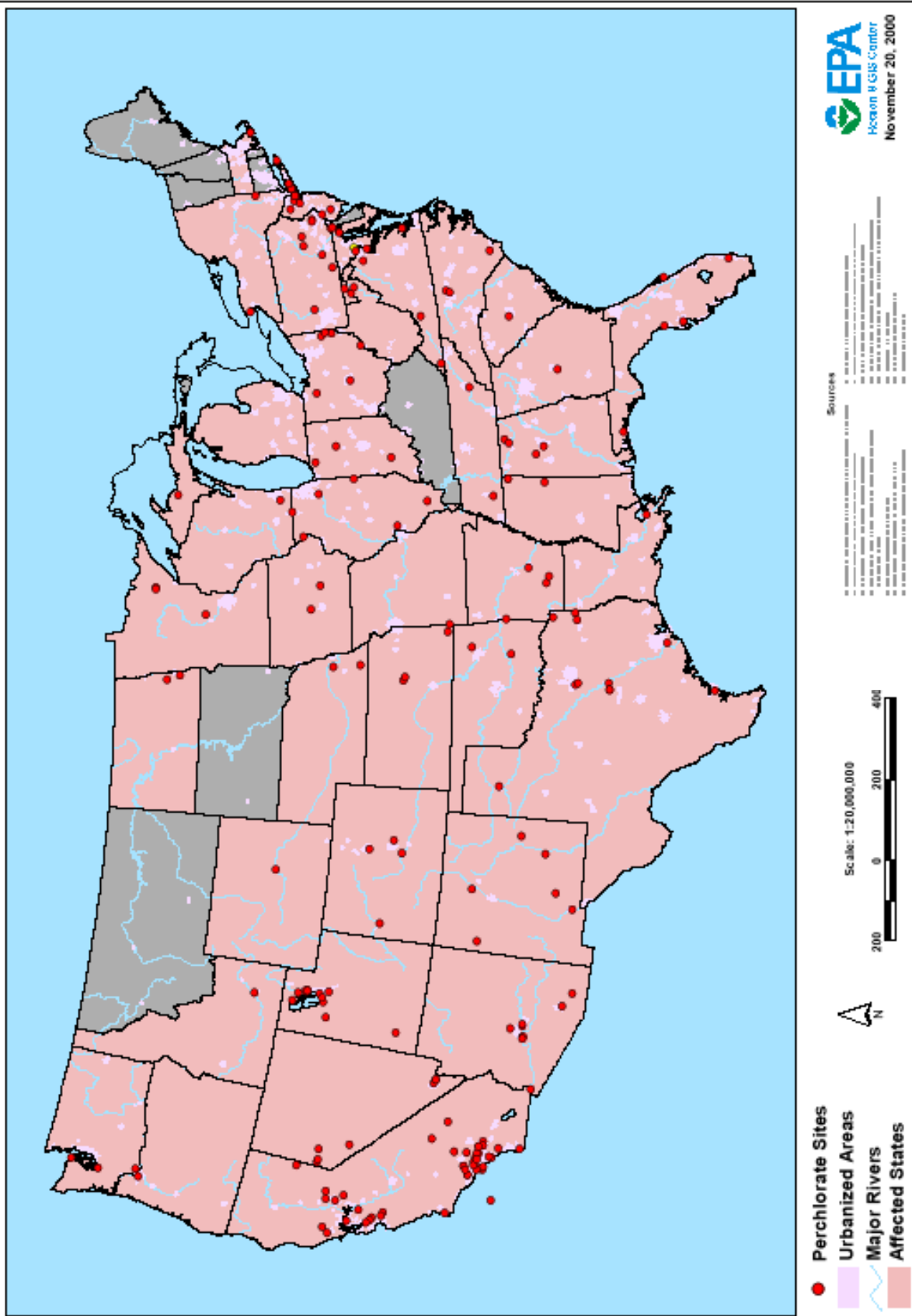


TABLE 1. OCURENCE AND POTENTIAL SOURCES OF PERCHLORATE
RELEASES TO THE ENVIRONMENT as of NOVEMBER, 2000 ^(a)

		Suspected Source	Type of Contamination	Max. Conc. ppb
AZ	Apache Nitrogen Products Benson, AZ	Explosives Manufacturing	Monitoring Well	670
AZ	Aerodyne Gila River Ind. Res., Chandler, AZ	Propellant Testing	Monitoring Well	18
AZ	Davis Monthan AFB Tucson, AZ	Explosives/Propellant Disposal	Soil	Not Confirmed
AZ	Unidynamics Phoenix Inc. Phoenix Goodyear Aripport Goodyear, AZ	Explosives/Ordnance Manufacturing	Monitoring Well	80
AZ	Universal Propulsion Phoenix, AZ	Rocket Manufacturing	Soil	--
AZ	Unidynamics Phoenix, Inc. White Tanks Disposal Area Maricopa County, AZ	Explosives/Ordnance Disposal	Public Water Supply Well (Unconfirmed Report) Soil	(4) --
AR	Atlantic Reseach East Camden, AR	Rocker Manufacturing Disposal – Open burn/Open detonation	Monitoring Well Surface Water Soil	1,500 480,000 --
CA	Aerojet General also affects Mather AFB Rancho Cordova, CA	Rocket Manufacturing	Public Water Supply Well Monitoring Well	260 640,000
CA	Alpha Explosives Lincoln, CA	Explosives Manufacturing	Monitoring Well Reported in Surface Water	67,000
CA	Boeing/Rocketdyne, NASA at Santa Susana Field Lab USDOE Santa Susana, CA	Rocket Research, Testing and Production	Monitoring Well	750
CA	Edwards AFB Jet Propulsion Lab, North Base Edwards, CA	Rocket Research	Monitoring Well	300
CA	El Toro Marine Corps Air Station	Explosives Disposal	Monitoring Well	380
CA	Lawrence Livermore National Laboratory Site 300 Tracy, CA	U.S. Dept. of Energy Explosives Research	Monitoring Well	84
CA	Lockheed Propulsion Upper Santa Ana Valley Redlands, CA	Rocket Manufacturing	Public Water Supply Well	87
CA	NASA-Jet Propulsion Lab Raymond Basin Pasadena, CA	Rocket Research	Public Water Supply Well	54
CA	Rialto, CA	Fireworks Facility (?)	Public Water Supply Well	811
CA	San Fernando Valley, Glendale, CA	Grand Central Rocket (?)Rocket Manufacturing	Monitoring Well	84
CA	San Gabriel Valley Baldwin Park, CA	Aerojet Rocket Manufacturing	Public Water Supply Well Monitoring Well	159 2,180

CA	San Nicholas Island Ventura Co., CA	U.S. Navy Firing Range	Public Water Supply (Springs)	12
CA	UTC (United Technologies) San Jose, CA	Rocket Testing	Monitoring Well	180,000
CA	Whittaker-Bermite Ordnance Santa Clarita, CA	Ordnance Manufacturing	Public Water Supply Well	47
CA	Whittaker Ordnance Hollister, CA	Ordnance Manufacturing	Private Well Monitoring Well	810 88
IN	American Water Works Service Greenwood, IN	Unknown source	Public Water Supply Well (Unconfirmed Report)	(4)
IA	American Water Works Service Clinton, VA	Unknown Source	Public Water Supply Well (Unconfirmed Report)	(6)
IA	Ewart, IA	Unknown Source	Monitoring Well	29
IA	Napier	Agriculture(?)	Monitoring Well	10
KS	Herington, KS	Ammunition Facility	Monitoring Well	9
MA	Massachusetts Military Res. Barnstable Co., MA	Disposal – Open burn/ Open detonation	Monitoring Well	100
MD	Naval Surface Warfare Center Indian Head, MD	Propellant Handling	Waste Discharge to Surface Water	>1,000
MD	White Oak Fed. Rs. Ctr. (Naval Surface Warfare Ctr.) WhieOak, MD	Propellant Handling	Monitoring Well	72
MO	ICI Explosives Joplin, MO	Explosives Facility	Monitoring Well	107,000
NE	Lewiston, NE	Agricultural Chemical Facility	Shallow Private Well	5
NE	Mead, NE	Fireworks Facility	Monitoring Well	24
NV	Kerr-McGee/BMI Henderson, NV	Chemical Manufacturing	Public Water Supply Monitoring Well Surface Well	16 3,700,000 120,000
NV	PEPCON Henderson, NV	Chemical Manufacturing	Monitoring Well	600,000
NM	American Water Works Service Clovis, NM	Unknown	Public Water Supply Well (Unconfirmed Report)	(4)
NM	Fort Wingate Depot Activity Gallup, NM	Explosives Disposal	Monitoring Well	2,860
NM	Holloman AFB Alamogondo, NM	Rocket Testing	Monitoring Well Seasonal Surface Water Soil	40 16,000
NM	Los Alamos National Lab Los Alamos, NM	U.S. Dept. of Energy Lab Chemical	Public Water Supply Well Monitoring Well Deep Borehold Water	3 220 1,662
NM	Melrose Air Force Range Melrose, NM	Explosives	Public Water Supply Well	25
NM	White Sands Missile Range White Sands, NM	Rocket Testing	Monitoring Well Soil	21,000
NY	Westhampton Suffolk County, NY	Unknown Source, Possibly Agricultural	Public Water Supply Well Monitoring Well	16 3370
NY	Yaphank Suffolk County, NY	Unknown Source	Private Well Monitoring Well	24 122

PA	American Water Works Service Yardley, PA	Unknown	Public Water Supply Well (Unconfirmed Report)	(5)
TX	Longhorn Army Ammunition Depot Kamak, TX	Propellant Handling	Monitoring Well Reported in Surface Water Soil	169,000 -- --
TX	McGregor Naval Weapons Plant McGregor, TX	Propellant Handling	Monitoring Well Reported in Surface Water Soil	91,000 -- --
TX	PANTEX Plant (USDOE) Amarillo, TX	Explosives	Monitoring Well	5
TX	Red River Army Depot Texarkana, TX	Propellant Handling	Monitoring Well	80
UT	Alliant Tech Systems Magna, UT	Rocket Manufacturing	Public Water Supply Well	16
UT	Thiokol Promontory, UT	Rocket Manufacturing	Water Supply Well (Inactive)	42
WA	Camp Booneville near Vancouver, WA	Explosives/Propellant Disposal	Soil	--
WV	Allegheny Ballistics Lab Rocket Center, WV	Rocket Research, Production, Open burn/Open detonation	Surface Discharge of Groundwater Extraction	400

(a) Information from Mayer (2000). All reports have been confirmed by federal, state or county agencies except where noted. Soil concentrations are not listed.

Appendix 2—Seawater Temperatures

Water temperature data from offshore bouy stations. Statistics are calculated from year 2000 data. Locations are typically miles offshore. Shallow waters near shore may experience wider temperature variations.

Water Temperature near Alaska 46060 - N. P.WM. SOUND	Water Temperature near VAFB 46011 - SANTA MARIA	Water temperature near Cape Canaveral 41009 - CANAVERAL 20 NM East of Cape Canaveral, FL
60.58 N 146.83 W (60°34'45"N 146°50'04" W) Source NOAA	34.88 N 120.87 W (34°52'51"N 120°52'10" W) Source NOAA	28.50 N 80.18 W (28°30'01"N 80°10'03"W)
°C °F	°C °F	°C °F
Min 2.6 36.7	Min 9.9 49.8	Min 19.5 67.1
Max 16.2 61.2	Max 18.5 65.3	Max 30.7 87.3
Average 8.3 47.0	Average 13.8 56.9	Average 25.3 77.6
Std dev 3.59 6.46	Std dev 1.84 3.31	Std dev 2.50 4.50
Station 46060 is owned and maintained by National Data Buoy Center 3-meter discus buoy Sea temp depth: 0.6 m below site elevation Water depth: 457.2 m	Station 46011 is owned and maintained by National Data Buoy Center 3-meter discus buoy Sea temp depth: 0.6 m below site elevation Water depth: 185.9 m	Station 41009 is owned and maintained by National Data Buoy Center 6-meter NOMAD buoy Sea temp depth: 1m below site elevation Water depth: 42.0 m

Source: National Data Bouy Center

LABORATORY OPERATIONS

The Aerospace Corporation functions as an “architect-engineer” for national security programs, specializing in advanced military space systems. The Corporation's Laboratory Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual organizations:

Electronics and Photonics Laboratory: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, data storage and display technologies; lasers and electro-optics, solid state laser design, micro-optics, optical communications, and fiber optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Space Materials Laboratory: Evaluation and characterizations of new materials and processing techniques: metals, alloys, ceramics, polymers, thin films, and composites; development of advanced deposition processes; nondestructive evaluation, component failure analysis and reliability; structural mechanics, fracture mechanics, and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle fluid mechanics, heat transfer and flight dynamics; aerothermodynamics; chemical and electric propulsion; environmental chemistry; combustion processes; space environment effects on materials, hardening and vulnerability assessment; contamination, thermal and structural control; lubrication and surface phenomena.

Space Science Applications Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; infrared surveillance, imaging, remote sensing, and hyperspectral imaging; effects of solar activity, magnetic storms and nuclear explosions on the Earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation, design fabrication and test; environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes.

Center for Microtechnology: Microelectromechanical systems (MEMS) for space applications; assessment of microtechnology space applications; laser micromachining; laser-surface physical and chemical interactions; micropropulsion; micro- and nanosatellite mission analysis; intelligent microinstruments for monitoring space and launch system environments.

Office of Spectral Applications: Multispectral and hyperspectral sensor development; data analysis and algorithm development; applications of multispectral and hyperspectral imagery to defense, civil space, commercial, and environmental missions.